

STATISTICAL THEORY OF THE ATOM IN MOMENTUM SPACE

VERENA VON CONTA AND HEINZ SIEDENTOP

ABSTRACT. We investigate the momentum energy functional for atoms found by Englert [1] who also discussed the relation to the Thomas-Fermi functional. We give a proof for the fact that the momentum functional yields upon minimization the same value as the well known Thomas-Fermi functional. In fact, we show an explicit relation between the minimizers of the functionals.

1. INTRODUCTION

Englert [1] derived an energy functional for the ground state energy of an atom with atomic number Z depending on the momentum density τ . In units where $\hbar = 2m = 1$ it reads for fermions having q spin states each

$$(1) \quad \mathcal{E}_{\text{mTF}}(\tau) := \mathcal{K}_m(\tau) - \mathcal{A}_m(\tau) + \mathcal{R}_m(\tau) = \int_{\mathbb{R}^3} \xi^2 \tau(\xi) d\xi - \frac{3}{2} \gamma^{-\frac{1}{2}} Z \int_{\mathbb{R}^3} \tau(\xi)^{2/3} d\xi \\ + \frac{3}{4} \gamma^{-\frac{1}{2}} \int_{\mathbb{R}^3} d\xi \int_{\mathbb{R}^3} d\xi' (\tau_{<}(\xi, \xi') \tau_{>}(\xi, \xi')^{2/3} - \frac{1}{5} \tau_{<}(\xi, \xi')^{5/3})$$

where $\gamma := (6\pi^2/q)^{2/3}$ is the Thomas-Fermi constant, $\tau_{<}(\xi, \xi') := \min\{\tau(\xi), \tau(\xi')\}$, and $\tau_{>}(\xi, \xi') := \max\{\tau(\xi), \tau(\xi')\}$.

This is to be compared with the well known Thomas-Fermi functional in position space (Lenz [2])

$$(2) \quad \mathcal{E}_{\text{TF}}(\rho) := \mathcal{K}(\rho) - \mathcal{A}(\rho) + \mathcal{R}(\rho) = \frac{3}{5} \gamma \int_{\mathbb{R}^3} \rho(x)^{5/3} dx - \int_{\mathbb{R}^3} \frac{Z}{|x|} \rho(x) dx + D[\rho]$$

where $D[\rho]$ is the quadratic form of

$$(3) \quad D(\rho, \sigma) := \frac{1}{2} \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} dy \frac{\overline{\rho(x)\sigma(y)}}{|x-y|},$$

the electro-static interaction energy of the charge density ρ with the charge density σ . Mathematically this functional has been studied in details by Lieb and Simon [4, 5] and Lieb [3]. The aim of this article is to establish the basic mathematical properties of \mathcal{E}_{mTF} .

2. DOMAIN OF DEFINITION OF THE MOMENTUM FUNCTIONAL

Theorem 1. *The functional \mathcal{E}_{mTF} is well defined on real valued functions in $L^1(\mathbb{R}^3, (1 + \xi^2)d\xi)$.*

Proof. The first summand of $\mathcal{E}_{\text{mTF}}(\tau)$ is obviously well defined. The finiteness of the second summand follows from

$$(4) \quad \int |\tau|^{2/3} \leq \left(\int \frac{d\xi}{(1 + \xi^2)^2} \right)^{1/3} \left(\int d\xi (1 + \xi^2) |\tau(\xi)| \right)^{2/3} < \infty$$

by Hölder's inequality. The third summand, the electron-electron interaction energy consists of two parts. Now,

$$(5) \quad \iint d\xi d\xi' |\tau_{>}(\xi, \xi')|^{2/3} |\tau_{<}(\xi, \xi')| \leq 2 \int d\xi |\tau(\xi)|^{2/3} \int d\xi' |\tau(\xi')|$$

which is finite by the previous argument. \square

We write

$$\begin{aligned} \mathcal{I} &:= \{\rho \in L^1(\mathbb{R}^3) \cap L^{5/3}(\mathbb{R}^3) \mid \rho \geq 0\}, \\ \mathcal{I}_N &:= \{\rho \in \mathcal{I} \mid \int \rho \leq N\}, \\ \mathcal{I}_{\partial N} &:= \{\rho \in \mathcal{I} \mid \int \rho = N\} \end{aligned}$$

for densities in position space and

$$\begin{aligned} \mathcal{J} &:= \{\tau \in L^1(\mathbb{R}^3, (1 + \xi^2)d\xi) \mid \tau \geq 0\}, \\ \mathcal{J}_N &:= \{\tau \in \mathcal{J} \mid \int \tau \leq N\}, \\ \mathcal{J}_{\partial N} &:= \{\tau \in \mathcal{J} \mid \int \tau = N\} \end{aligned}$$

for densities in momentum space.

3. RELATION BETWEEN POSITION AND MOMENTUM FUNCTIONAL

In this section we will see that each summand of \mathcal{E}_{mTF} is obtained from the corresponding term of \mathcal{E}_{TF} by mere substitution – at least for spherically symmetric decreasing densities. To this end we set

$$(6) \quad S : L^1(\mathbb{R}^3) \rightarrow L^1(\mathbb{R}^3)$$

$$(7) \quad \tau \mapsto \rho$$

where for all $x \in \mathbb{R}^3$

$$(8) \quad \rho(x) := \frac{q}{(2\pi)^3} \int_{|x| < \gamma^{1/2} |\tau(\xi)|^{1/3}} d\xi.$$

Moreover, given $\rho \in L^1(\mathbb{R}^3)$ we define its Fermi radius r by

$$(9) \quad r(s) := \sup\{|y| \mid \gamma^{1/2} |\rho(y)|^{1/3} \geq s\}.$$

This allows to define the operator

$$(10) \quad T : L^1(\mathbb{R}) \rightarrow L^1(\mathbb{R}^3)$$

$$(11) \quad \rho \mapsto \tau$$

where for all $\xi \in \mathbb{R}^3$

$$(12) \quad \tau(\xi) := \gamma^{-3/2} r(|\xi|)^3.$$

Our main result is

Theorem 2.

1. For all $N \geq 0$ we have $\inf \mathcal{E}_{\text{mTF}}(\mathcal{J}_{\partial N}) = \inf \mathcal{E}_{\text{TF}}(\mathcal{I}_{\partial N})$.
2. Assume $N \leq Z$ and ρ_m the minimizer of \mathcal{E}_{TF} on $\mathcal{I}_{\partial N}$. Then $T(\rho_m)$ is the unique minimizer of \mathcal{E}_{mTF} on $\mathcal{J}_{\partial N}$.
3. For $N > Z$ there exists no minimizer of \mathcal{E}_{mTF} on $\mathcal{J}_{\partial N}$.
4. There exist a unique minimizer τ_m of \mathcal{E}_{mTF} on \mathcal{J}_N . Moreover, $\tau_m \in \mathcal{J}_{\partial \min\{N, Z\}}$.

To prove Theorem 2 we need a few preliminary results on the transforms S and T and the way they relate the two functionals \mathcal{E}_{TF} and \mathcal{E}_{mTF} .

Lemma 1.

1. The operators S and T are isometric on L^1 .
2. All elements in the image of S or T are spherically symmetric, non-negative, and decreasing.
3. For every spherically symmetric decreasing $\tau \in \mathcal{J}$

$$\mathcal{E}_{\text{mTF}}(\tau) = \mathcal{E}_{\text{TF}} \circ S(\tau).$$

4. For every spherically symmetric decreasing $\rho \in \mathcal{I}$

$$\mathcal{E}_{\text{mTF}} \circ T(\rho) = \mathcal{E}_{\text{TF}}(\rho).$$

Proof. 1. The claim for S follows easily by direct computation interchanging the x and ξ integration.

To treat T we may, without loss of generality, assume $\rho \geq 0$. Moreover,

$$(13) \quad |x| < r(|\xi|) \Rightarrow \gamma^{1/2} \rho(x)^{1/3} \geq |\xi|$$

by definition of r and since ρ is monotonically decreasing. Furthermore, the definition of r provides

$$(14) \quad |x| \leq r(|\xi|) \Leftarrow \gamma^{1/2} \rho(x)^{1/3} \geq |\xi|.$$

We have

$$(15) \quad \|T(\rho)\|_1 = \frac{3}{4\pi\gamma^{3/2}} \int d\xi \int_{|x| < r(|\xi|)} dx = \frac{3}{4\pi\gamma^{3/2}} \int dx \int_{|x| < r(|\xi|)} d\xi.$$

By (13) we get the estimate

$$(16) \quad \|T(\rho)\|_1 \leq \frac{3}{4\pi\gamma^{3/2}} \int dx \int_{\gamma^{1/2} \rho(x)^{1/3} \geq |\xi|} d\xi = \int dx \rho(x).$$

On the other hand, if we allow for \leq instead of strict inequality on the integration constraints in (15) we can also reverse the inequality in (16) using (14).

2. The claims are obvious from the definitions.

3. We treat each term of the energy functional individually. We start with the potential terms. Both follow by explicit calculation which we exhibit here only for the interaction potential since the external potential is an easy variant of it. Given a radius $a > 0$ we set K_a to be the characteristic function of the ball of radius a centered at the origin, i.e.,

$$(17) \quad K_a(x) := \chi_{\{x \in \mathbb{R}^3 \mid |x| < a\}}(x) = \begin{cases} 1 & |x| < a \\ 0 & |x| \geq a \end{cases}.$$

We get

$$(18) \quad \mathcal{R}(S(\tau)) = \left(\frac{q}{(2\pi)^3} \right)^2 \iint d\xi d\eta D(K_{\gamma^{1/2}\tau(\xi)^{1/3}}, K_{\gamma^{1/2}\tau(\eta)^{1/3}})$$

$$(19) = \left(\frac{3}{4\pi} \right)^2 \gamma^{-1/2} \iint d\xi d\eta D(K_{\sqrt[3]{\tau_{<}(\xi, \eta)}}, K_{\sqrt[3]{\tau_{>}(\xi, \eta)}})$$

$$(20) = \frac{9}{(4\pi)^2 \sqrt{\gamma}} \iint D[K_{\sqrt[3]{\tau_{<}(\xi, \eta)}}] + D(K_{\sqrt[3]{\tau_{<}(\xi, \eta)}}, K_{\sqrt[3]{\tau_{>}(\xi, \eta)}} - K_{\sqrt[3]{\tau_{<}(\xi, \eta)}}) d\xi d\eta$$

$$(21) = \frac{9}{(4\pi)^2 \sqrt{\gamma}} \iint D[K_1] \tau_{<}(\xi, \eta)^{5/3} + \frac{4\pi}{3} \tau_{<}(\xi, \eta) 2\pi (\tau_{>}(\xi, \eta)^{2/3} - \tau_{<}(\xi, \eta)^{2/3}) d\xi d\eta$$

$$(22) = \frac{3}{4} \gamma^{-1/2} \iint \tau_{<}(\xi, \eta) \tau_{>}(\xi, \eta)^{2/3} - \frac{1}{5} \tau_{<}(\xi, \eta)^{5/3} d\xi d\eta$$

where we used the scaling properties of D and Newton's theorem [6].

The kinetic energy transforms as

$$\begin{aligned}
 \mathcal{K}(S(\tau)) &= \frac{3}{5}\gamma \int dx S(\tau)(x)^{5/3} \\
 (23) \quad &= 3\gamma \int dx \int_{t \leq S(\tau)(x)^{1/3}} dt t^4 = \frac{3}{4\pi}\gamma \int d\xi \xi^2 \int_{|\xi|^3 \leq S(\tau)(x)} dx.
 \end{aligned}$$

Given that $\frac{3}{4\pi} \int_{|x| < \tau(\eta)^{1/3}} d\eta \geq |\xi|^3$ implies $\tau(\xi)^{1/3} \geq |x|$, we have

$$(24) \quad \frac{3}{5}\gamma \int dx S(\tau)(x)^{5/3} \leq \frac{3}{4\pi}\gamma \int d\xi \xi^2 \int_{|x| \leq \gamma^{1/2}\tau(\xi)^{1/3}} dx = \int \xi^2 \tau(\xi) d\xi.$$

Suppose $\frac{3}{4\pi} \int_{|x| < \tau(\eta)^{1/3}} d\eta \geq |\xi|^3$ would not imply $\tau(\xi)^{1/3} \geq |x|$. Then

$$(25) \quad |\xi|^3 \leq \frac{3}{4\pi} \int_{|x| < \tau(\eta)^{1/3}} d\eta < \frac{3}{4\pi} \int_{\tau(\xi) < \tau(\eta)} d\eta \leq \frac{3}{4\pi} \int_{|\xi| > |\eta|} d\eta = |\xi|^3$$

where we used in the last inequality that τ is spherically symmetric and decreasing.

On the other hand, $\frac{3}{4\pi} \int_{|x| < \tau(\eta)^{1/3}} d\eta \geq |\xi|^3$ follows from $\tau(\xi)^{1/3} > |x|$ as

$$(26) \quad |\xi|^3 = \frac{3}{4\pi} \int_{|\eta| \leq |\xi|} d\eta \leq \frac{3}{4\pi} \int_{\tau(\xi) \leq \tau(\eta)} d\eta \leq \frac{3}{4\pi} \int_{|x| < \tau(\eta)^{1/3}} d\eta$$

using again that τ is spherically symmetric and decreasing in the first inequality. Thus we can reverse the inequality in (24), i.e.,

$$(27) \quad \frac{3}{5}\gamma \int dx S(\tau)(x)^{5/3} \geq \frac{3}{4\pi}\gamma \int d\xi \xi^2 \int_{|x| < \gamma^{1/2}\tau(\xi)^{1/3}} dx = \int \xi^2 \tau(\xi) d\xi.$$

4. To prove that $\mathcal{E}_{\text{mTF}} \circ T(\rho) = \mathcal{E}_{\text{TF}}(\rho)$ we proceed as in 3. We begin with the kinetic energy:

$$\begin{aligned}
 (28) \quad \mathcal{K}_m(T(\rho)) &= \int \xi^2 \gamma^{-3/2} r(|\xi|)^3 d\xi = \frac{3}{4\pi} \gamma^{-3/2} \int d\xi \xi^2 \int_{|x| < r(|\xi|)} dx \\
 &= \frac{3}{4\pi} \gamma^{-3/2} \int d\xi \xi^2 \int_{|\xi| \leq \gamma^{1/2}\rho(x)^{1/3}} dx = \mathcal{K}(\rho)
 \end{aligned}$$

where we used (13) and (14) in the penultimate identity.

We skip again \mathcal{A}_m and go directly to \mathcal{R}_m . Set $r_<(|\xi|, |\eta|) := \min\{r(|\xi|), r(|\eta|)\}$ and $r_>(|\xi|, |\eta|) := \max\{r(|\xi|), r(|\eta|)\}$. Then

$$(29) \quad \mathcal{R}_m(T(\rho)) = \left(\frac{3}{4\pi}\right)^2 \gamma^{-1/2} \iint d\xi d\eta D(K_{\gamma^{-1/2}r_<(|\xi|, |\eta|)}, K_{\gamma^{-1/2}r_>(|\xi|, |\eta|)})$$

adapting the steps (22) to (19). Making the term explicit and scaling $\gamma^{-1/2}$ out yields

$$\begin{aligned}
 (30) \quad \mathcal{R}_m(T(\rho)) &= \frac{1}{2} \left(\frac{3}{4\pi}\right)^2 \gamma^{-3} \iint \frac{dx dy}{|x - y|} \int_{|x| < r(|\xi|)} d\xi \int_{|y| < r(|\eta|)} d\eta \\
 &= \frac{1}{2} \left(\frac{3}{4\pi}\right)^2 \gamma^{-3} \iint \frac{dx dy}{|x - y|} \int_{|\xi| \leq \gamma^{1/2}\rho(x)^{1/3}} d\xi \int_{|\eta| \leq \gamma^{1/2}\rho(y)^{1/3}} d\eta = \mathcal{R}(\rho)
 \end{aligned}$$

where we used (13) and (14) again. □

4. THE ENERGY UNDER REARRANGEMENT

The fact that $\mathcal{E}_{\text{TF}}(\rho)$ decreases under spherical symmetric rearrangement of ρ is well known (Lieb [3, Theorem 2.12]). The same result holds for the momentum functional:

Lemma 2. *For $\tau \in \mathcal{J}$,*

$$(31) \quad \mathcal{E}_{\text{mTF}}(\tau^*) \leq \mathcal{E}_{\text{mTF}}(\tau)$$

where τ^* is the spherically symmetric rearrangement of τ .

Proof. The attraction \mathcal{A}_m is obviously invariant under rearrangement. The repulsion \mathcal{R}_m is – by definition – a superposition of rearranged terms only, i.e., is also trivially invariant.

Now, $\mathcal{K}_m(\tau) = \int_0^\infty dt \int \xi^2 \chi_{\{\xi \in \mathbb{R}^3 \mid \tau(\xi) > t\}}(\xi) d\xi$. Thus it suffices to show that for any $A \subset \mathbb{R}^3$ with finite measure

$$\int \xi^2 \chi_A(\xi) d\xi \geq \int \xi^2 \chi_{A^*}(\xi) d\xi = \int \xi^2 K_R(\xi) d\xi$$

where R is defined by $|A| = (4\pi/3)R^3$, i.e., the radius of the ball $A^* := B_R(0)$ centered at the origin which has the same volume as A . Now define $B := A^* \setminus A$, $C := A \setminus A^*$, and $D := A \cap A^*$. Then $|B| = |C|$, and thus

$$\begin{aligned} \int_{A^*} \xi^2 d\xi &= \int_B \xi^2 d\xi + \int_D \xi^2 d\xi \leq R^2 \int_B d\xi + \int_D \xi^2 d\xi \leq \int_C \xi^2 d\xi + \int_D \xi^2 d\xi \\ &= \int_A \xi^2 d\xi. \end{aligned}$$

□

5. CONVEXITY

Although, \mathcal{K}_m and $-\mathcal{A}_m$ are convex in τ , the third summand \mathcal{R}_m of \mathcal{E}_{mTF} is not. We circumvent this problem with a simple substitution $\mathcal{E}_s(\tilde{\tau}) := \mathcal{E}_{\text{mTF}}(\tilde{\tau}^{3/2})$ for $\tilde{\tau} \in L^{3/2}(\mathbb{R}^3, (1 + \xi^2)d\xi)$ and $\tilde{\tau} \geq 0$.

Lemma 3. *The functional \mathcal{E}_s is strictly convex.*

Proof. The first summand is obviously strictly convex, the second is linear. It remains to show the convexity of the repulsion term. Since the Heaviside function

θ is the derivative of the positive part $[\cdot]_+$, we get

$$\begin{aligned}
& \iint d\xi d\eta \left(\tilde{\tau}_{<}(\xi, \eta)^{3/2} \tilde{\tau}_{>}(\xi, \eta) - \frac{1}{5} \tilde{\tau}_{<}(\xi, \eta)^{5/2} \right) \\
&= \text{const} \iint \frac{dx dy}{|x - y|} \int_{\tilde{\tau}(\xi) > |x|^2} d\xi \int_{\tilde{\tau}(\eta) > |y|^2} d\eta \\
&= \text{const} \iint d\xi d\eta \int_0^\infty dr r^2 \int_0^\infty ds s^2 \frac{\theta(\tilde{\tau}(\xi) - r^2) \theta(\tilde{\tau}(\eta) - s^2)}{\max\{r, s\}} \\
&= \text{const} \iint d\xi d\eta \int_0^\infty dr r \left(-\frac{d}{dr} [\tilde{\tau}(\xi) - r^2]_+ \right) \\
&\quad \times \left(\frac{1}{r} \int_0^r ds s \left(-\frac{d}{ds} [\tilde{\tau}(\eta) - s^2]_+ \right) + \int_r^\infty ds \left(-\frac{d}{ds} [\tilde{\tau}(\eta) - s^2]_+ \right) \right) \\
&= \text{const} \iint d\xi d\eta \int_0^\infty dr r \frac{d}{dr} [\tilde{\tau}(\xi) - r^2]_+ \\
&\quad \times \left(\frac{1}{r} s [\tilde{\tau}(\eta) - s^2]_+ \Big|_{s=0}^{s=r} - \frac{1}{r} \int_0^r ds [\tilde{\tau}(\eta) - s^2]_+ - [\tilde{\tau}(\eta) - r^2]_+ \right) \\
&= \text{const} \iint d\xi d\eta \int_0^\infty dr \frac{d}{dr} [\tilde{\tau}(\xi) - r^2]_+ \left(- \int_0^r ds [\tilde{\tau}(\eta) - s^2]_+ \right) \\
&= \text{const} \iint \left(- [\tilde{\tau}(\xi) - r^2]_+ \int_0^r ds [\tilde{\tau}(\eta) - s^2]_+ \right) \Big|_{r=0}^{r=\infty} \\
&\quad + \int_0^\infty dr [\tilde{\tau}(\xi) - r^2]_+ \frac{d}{dr} \left(\int_0^r ds [\tilde{\tau}(\eta) - s^2]_+ \right) d\xi d\eta \\
&= \text{const} \iint d\xi d\eta \int_0^\infty dr [\tilde{\tau}(\xi) - r^2]_+ [\tilde{\tau}(\eta) - r^2]_+ \\
&= \text{const} \int_0^\infty dr \left(\int d\xi [\tilde{\tau}(\xi) - r^2]_+ \right)^2
\end{aligned}$$

which is convex in $\tilde{\tau}$, q.e.d. \square

Now, we can prove Theorem 2.

Proof. 1. Since the energies of both – momentum and position – Thomas-Fermi functionals decrease under spherical symmetric rearrangement (Lemma 2 and [3, Theorem 2.12]) we can restrict both functionals to spherically symmetric decreasing densities ρ and τ as far as minimization is concerned. Since both S and T preserve the norm, Statement 3 of Lemma 1 implies that $\inf \mathcal{E}_{\text{mTF}}(\mathcal{J}_{\partial N}) \geq \inf \mathcal{E}_{\text{TF}}(\mathcal{I}_{\partial N})$ whereas Statement 4 implies the reverse inequality. This proves the first assertion of Theorem 2.

2. Since \mathcal{E}_{TF} has a unique minimizer ρ_m on $\mathcal{I}_{\partial N}$ (Lieb and Simon [5, Theorems II.14 and II.17]), it follows from the preceding step and Lemma 1, Statement 4, that $T(\rho_m)$ minimizes \mathcal{E}_{mTF} on $\mathcal{J}_{\partial N}$. It remains to show that there is no other minimizer of the momentum functional. This, however, follows from strict convexity of \mathcal{E}_s .

3. Suppose τ_m is a minimizer of \mathcal{E}_{mTF} on $\mathcal{J}_{\partial N}$ for some $N > Z$. Then $S(\tau_m)$ has to be a minimizer of \mathcal{E}_{TF} by Statement 1 and Lemma 1, Statement 3, but this does not exist [5].

4. Again, if τ_m minimizes \mathcal{E}_{mTF} on \mathcal{J}_N then $S(\tau_m)$ minimizes \mathcal{E}_{TF} on \mathcal{I}_N . Thus, $\int \tau_m = \int S(\tau_m) = \min\{Z, N\}$. Uniqueness of τ_m follows from the strict convexity of \mathcal{E}_s . \square

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MATHEMATISCHES INSTITUT, LUDWIG-MAXIMILIANS-UNIVERSITÄT MÜNCHEN, THERESIENSTRASSE
39, 80333 MÜNCHEN, GERMANY